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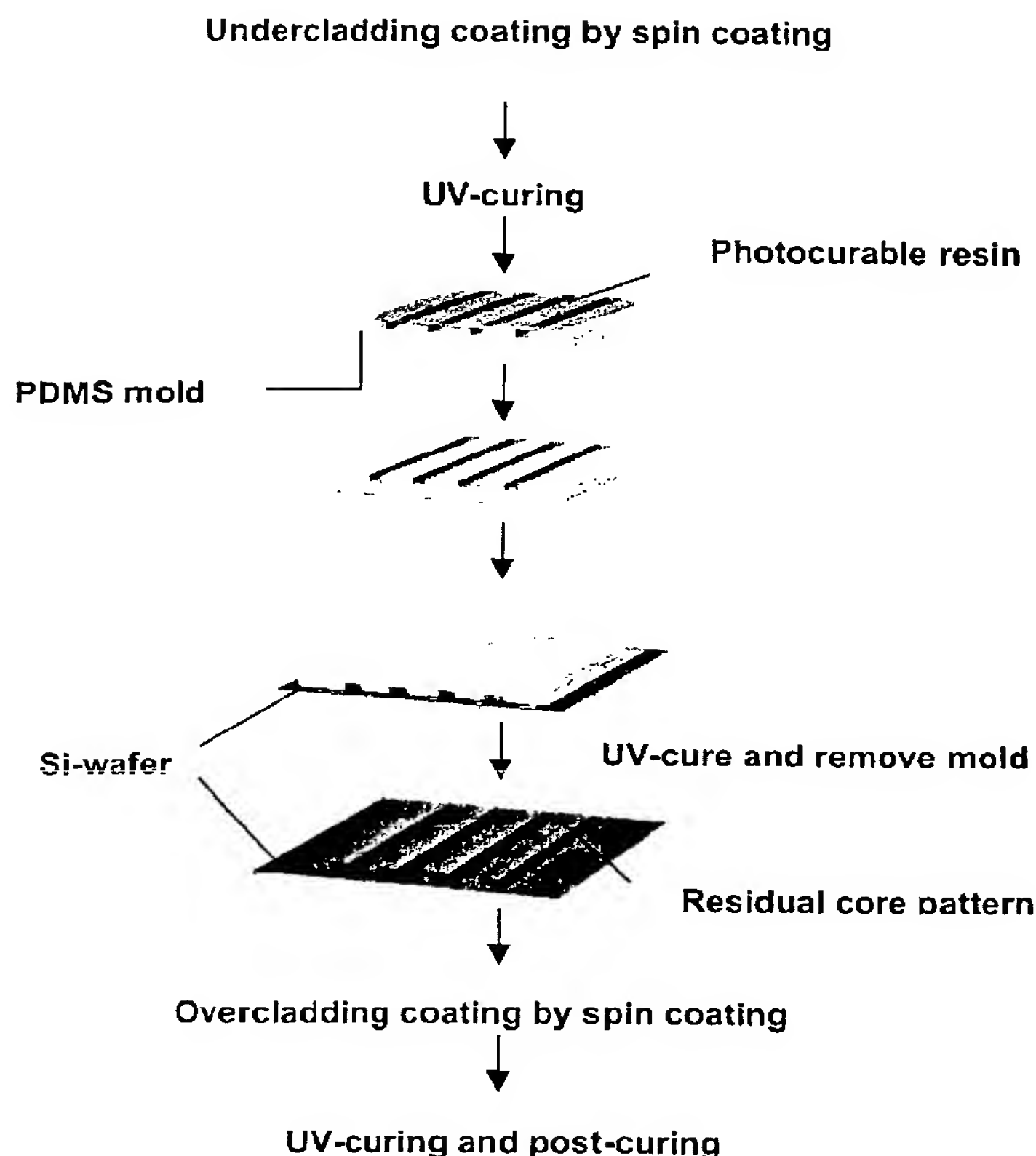
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(54) Title: **PHOTOCURABLE RESIN COMPOSITION FOR OPTICAL WAVEGUIDE AND OPTICAL WAVEGUIDE MADE OF THE SAME**



(57) Abstract: A photocurable resin composition useful for preparing an optical waveguide comprises a fluorinated photocurable urethane oligomer of formula (I), a reactive monomer and a photocurable initiator; wherein: R₁ is -CH₂O- or -CH₂(OCH₂CH₂)_mO-; R₂ is an aromatic or aliphatic hydrocarbon group containing from 6 to 100 carbon atoms; R₃ is an aromatic or aliphatic hydrocarbon group containing from 2 to 10 carbon atoms; and R₄ is a (meth)acrylate or epoxy group.



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PHOTOCURABLE RESIN COMPOSITON FOR OPTICAL WAVEGUIDE AND OPTICAL WAVEGUIDE MADE OF THE SAME

FIELD OF THE INVENTION

5 The present invention relates to a photocurable resin composition having improved thermal stability and optical transmittance, and optical waveguides made of the same via micro-molding technique.

BACKGROUND OF THE INVENTION

10 In the field of telecommunications, development of optical waveguide has been recognized as a critical issue enabling large capacity communications. Glass or other inorganic crystalline materials have conventionally been used as materials for producing optical communication parts such as an optical waveguide. These materials, however, have the
15 disadvantages of high cost and difficulty in processing.

 In recent years, polymer materials, such as PMMA (polymethyl methacrylate) and PS (polystyrene), have become more popular thanks to their lower cost and easier processing ability than glass or other inorganic crystalline materials. Use of such material can provide a film-type optical
20 waveguide with wider area and higher flexibility than the conventional ones. Such use also makes it possible to obtain a functional optical waveguide by incorporating functional compounds or functional groups into such polymer materials.

 However, PMMA and PS show absorption ascribable to C-H bonds in
25 their molecules in the near-infrared region, i.e., 1.0~1.8 μ m; and thus deuterated or fluorinated PMMA (that is, PMMA whose hydrogen atoms are substituted with deuterium or fluorine atoms) has been developed. Such deuterated or fluorinated PMMA shows absorption in the far-infrared region as shifted from the near-infrared region.

30 The above-described PMMA, PS and deuterated or fluorinated PMMA constituting a core of the optical waveguide, however, have low glass transition temperatures. For instance, both PMMA and deuterated PMMA have a glass transition temperature of about 100°C, so that these materials may easily be softened due to heat treatment, thereby having a low
35 thermal stability (see S. Imamura et al. Electronics Letters, 27, 1342, 1991).

 To solve the problem of low thermal stability, NTT Co., Ltd.

developed certain perfluorinated polyimide polymers. These polymers also suffer from a relatively high water absorption rate inducing an optical loss and polarization dependence due to high birefringence (see T. Matsuda et al., Electronics Letters, 29(3), 269, 1993).

5 Allied Signal Co. Ltd. developed UV-curable fluorinated acrylate having high thermal stability with a thermal decomposition temperature(T_d) as high as possible, e.g., 350°C, based on the photo-crosslinking property thereof. Such UV-curable fluorinated acrylate can have a controllable continuous refractive index in the range of 1.3 to 1.6 and low birefringence,
10 $\Delta n=0.0008$ and exhibit a low optical loss, e.g., 0.03 dB/cm and 0.05 dB/cm at the wavelengths of 1.3 and 1.55 μm , respectively.

Further, polyimide wherein hydrogen atoms are substituted with fluorine and chlorine has been developed; however, it has too high birefringence (see K. Han et al. Polym. Bull., 41, 455, 1998). Thermally
15 curable fluorinated polyarylene ether prepared by a heat-curing technique, having a good thermal stability but with a low productivity has also been developed (see J. Polym. Sci., Polym. Chem., 37, 235, 1999).

Accordingly, there still exists a need for photocurable resin compositions for optical waveguides with low optical loss and low
20 birefringence in the near-infrared region and low refractive index approaching traditional optical fibers.

Traditionally, waveguides have been fabricated by employing a process which comprises applying a set of masks in conformity with the shape of the waveguides on a coated core layer substrate, etching the
25 substrate to form a pattern by photolithography, removing the masks and attaching a layer of waveguide material. However, such a conventional method suffers from a long preparation time and difficulties in its etching process, especially in the preparation of a multimode waveguide in contrast to a single mode waveguide, as core materials have to be etched in such a
30 depth of 40 μm and more.

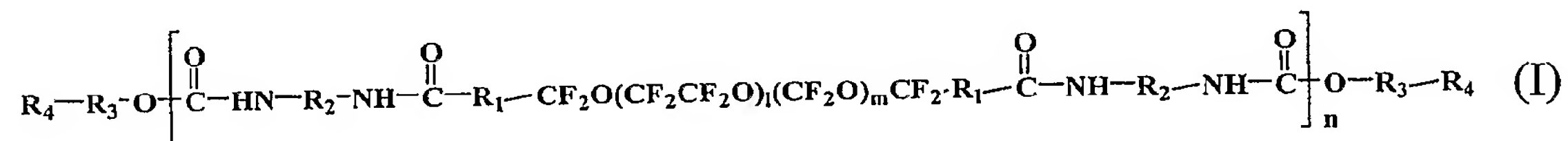
Accordingly, the present inventors have endeavored to develop a novel photocurable resin composition satisfying the above requirements, and optical waveguides made of the photocurable resin composition via micro-molding method.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a photocurable resin composition for use in producing optical waveguides having a low optical loss and birefringence as well as thermal stability.

5 It is another object of the present invention to provide optical waveguides made of said photocurable resin composition via micro-molding method.

In accordance with one aspect of the present invention, there is provided a photocurable resin composition for use in producing optical waveguides
10 comprising a fluorinated photocurable urethane oligomer of formula (I), a reactive monomer and a photocurable initiator:



wherein:

R_1 is $-\text{CH}_2\text{O}-$ or $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_m\text{O}-$;

15 R_2 is an aromatic or aliphatic hydrocarbon group containing from 6 to 100 carbon atoms;

R_3 is an aromatic or aliphatic hydrocarbon group containing from 2 to 10 carbon atoms; and

R_4 is a (meth)acrylate or epoxy group.

20

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become apparent from the following description thereof, when taken in conjunction with the accompanying drawings which respectively show:

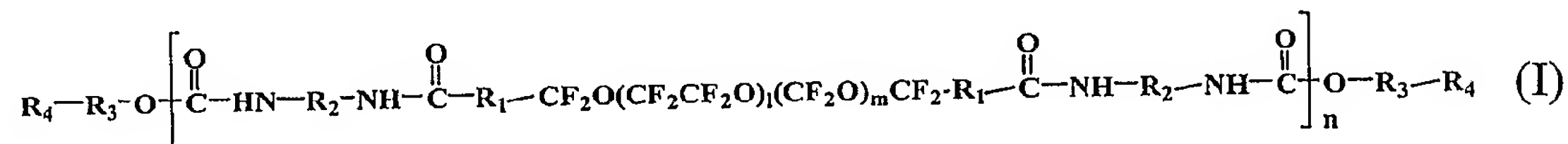
25 FIG. 1: a schematic processing diagram of an optical waveguide made of the inventive photocurable material via micro-transfer molding technique in accordance with the present invention; and

FIG. 2a and 2b: optical microscope and scanning electron microscope photographs for a cross-section of the wafer coated with the core layer
30 obtained in Example 11 of the present invention, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a photocurable resin composition for optical waveguides comprising a fluorinated photocurable urethane oligomer

of formula (I), a reactive monomer and a photocurable initiator:



wherein:

R₁ is -CH₂O- or -CH₂(OCH₂CH₂)_mO-;

5 R₂ is an aromatic or aliphatic hydrocarbon group containing from 6 to 100 carbon atoms;

R₃ is an aromatic or aliphatic hydrocarbon group containing from 2 to 10 carbon atoms; and

R₄ is a (meth)acrylate or epoxy group.

10

(A) Fluorinated photocurable urethane oligomer

A fluorinated photocurable urethane oligomer(A) in the composition of the present invention is prepared by using (a) a polyol, (b) a diisocyanate, (c) a hydroxy (meth)acrylate or a hydroxy epoxy, (d) an urethane reaction catalyst
15 and (e) a polymerization inhibitor.

(a) Polyol

A polyol used in the preparation of the fluorinated photocurable urethane oligomer(A) has a molecular weight in the range of 500 to 10,000, and preferably includes a fluorinated perfluoropolyether polyol or a
20 perfluoropolyether polyol having nonfluorinated polyether group at the end of perfluoropolyether chain. The polyol is used in an amount of from 20 to 80 wt% based on the amount of the oligomer composition.

(b) Diisocyanate

A diisocyanate used in the preparation of the fluorinated photocurable
25 urethane oligomer(A) is preferably selected from the group consisting of isophoron diisocyanate(IPDI), 1,6-hexane diisocyanate(HDI), 1,8-octamethylene diisocyanate, tetramethylxylene diisocyanate(TMXDI), 4,4'-dicyclohexylmethane diisocyanate(HMDI), 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate,
30 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, 4-bromo-6-methyl-1,3-phenylene diisocyanate, 4-chloro-6-methyl-1,3-phenylene diisocyanate, poly(1,4-butanediol) tolylene 2,4-diisocyanate terminated, poly(1,4-butanediol)isophorone diisocyanate terminated, poly(ethylene adipate)tolylene 2,4-diisocyanate terminated,

poly[1,4-phenylene diisocyanate-co-poly(1,4-butanol)] diisocyanate,
 poly(hexamethylene diisocyanate, poly(propylene glycol)tolylene
 2,4-diisocyanate terminated, poly(tetrafluoroethylene
 oxide-co-difluoromethylene oxide) α,ω -diisocyanate, 2,4-toluene
 5 diisocyanate, 2,5-toluene diisocyanate, 2,6-toluene diisocyanate,
 1,5-naphthalene diisocyanate and a mixture thereof.

The diisocyanate is used in an amount of from 10 to 50 wt% based on the amount of the oligomer composition.

(c) Hydroxy (meth)acrylate or hydroxy epoxy

10 A hydroxy (meth)acrylate or hydroxy epoxy used in the preparation of the fluorinated photocurable urethane oligomer(A) is a compound (c₁) having at least one (meth)acryloyl group and one hydroxy group or a compound (c₂) having at least one epoxy group and one hydroxy group.

Representative examples of compound c₁ include
 15 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate,
 2-hydroxybutyl(meth)acrylate), 1-hydroxybutyl(meth)acrylate,
 2-hydroxy-3-phenyloxypropyl(meth)acrylate,
 neopentylglycolmono(meth)acrylate, 4-hydroxycyclohexyl(meth)acrylate,
 1,6-hexanediolmono(meth)acrylate, pentaerythritolpenta(meth)acrylate,
 20 dipentaerythritolpenta(meth)acrylate, 2-methacryloxyethyl 2-hydroxypropyl
 phthalate, glycerin di(meth)acrylate, 2-hydroxy-3-acryloyloxy
 propyl(meth)acrylate, polycaprolactone polyol mono(meth)acrylate and a mixture thereof.

Representative examples of compound c₂ are glycidol and epoxidized
 25 tetrahydrobenzyl alcohol.

The hydroxy (meth)acrylate or hydroxy epoxy compound is used in an amount of from 5 to 50 wt% based on the amount of the oligomer composition.

(d) Urethane reaction catalyst

A urethane reaction catalyst is added in an amount of from 0.01 to 1
 30 wt% based on the amount of the oligomer composition during the reaction.

Representative examples of the urethane reaction catalyst include copper naphthenate, cobalt naphthenate, zinc naphthate, n-butyltinlaurate, trisethylamine, 2-methyltriethylenediamide and a mixture thereof.

(e) Polymerization inhibitor

35 A polymerization inhibitor is added in an amount of from 0.01 to 1 wt% based on the amount of the oligomer composition.

Representative examples of the polymerization initiator include hydroquinone, hydroquinonemonomethylether, para-benzoquinone, phenotiazine and a mixture thereof.

The photocurable oligomer(A) may be prepared by a conventional method, the preferred embodiment is as follows:

A fluorinated perfluoropolyether polyol or a perfluoropolyether polyol having nonfluorinated polyether group attached at the end of perfluoropolyether chain is added to a flask, and then, the moisture is removed under a reduced pressure. An isocyanate and an urethane reaction catalyst are added to the resulting mixture with stirring at 200 to 300 rpm. The reaction is carried out at a temperature ranging from 65 to 85°C for about 2 to 3 hrs, until the -OH peak is not observable by IR spectroscopy. At this time, an additional amount of the catalyst may be added to bring the reaction to completion. Then, a polymerization initiator and a hydroxy(meth)acrylate or hydroxy epoxy compound are added to the reaction mixture, the resulting mixture is heated at a temperature in the range of from 70 to 90°C, a suitable amount of the catalyst is added thereto and the reaction is carried out until the -NCO peak is not detectable by IR spectroscopy, to obtain a fluorinated photocurable urethane oligomer of the present invention.

The fluorinated photocurable urethane oligomer(A) of an average molecular weight in the range of 2,000 to 50,000 has a refractive index lower than that of a conventional urethane oligomer and an excellent optical transmittance at the 1.1 to 1.8 μ m wavelength range.

The fluorinated photocurable urethane oligomer(A) is employed in an amount of from 20 to 80 wt% based on the amount of the photocurable resin composition of the present invention.

(B) Photoreactive monomer

A photoreactive monomer used in the composition of the present invention may be a (meth)acrylate (B₁) having at least one (meth)acryloyl group or a photoreactive monomer (B₂) having at least one epoxy group.

The photoreactive monomer is classified into a monofunctional monomer, a difunctional monomer, a trifunctional monomer, etc., depending on the number of (meth)acryloyl or epoxy functions.

The (meth)acrylate (B₁) having at least one (meth)acryloyl group may be a fluorinated or nonfluorinated (meth)acrylate.

The monofunctional fluorinated (meth)acrylate includes 2-perfluorooctylethyl acrylate, 2-perfluorooctylethyl methacrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, trifluoroethyl methacrylate, 2-perfluoroalkylethyl acrylate and
 5 2-perfluoroalkylethyl methacrylate.

Representative examples of the monofunctional nonfluorinated (meth)acrylate are 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 1-hydroxybutyl(meth)acrylate, 2-hydroxy-3-phenoxypropyl(meth)acrylate,
 10 tetrahydrofurfuryl (meth)acrylate, isodecyl (meth)acrylate, 2-(2-ethoxyethoxy) ethyl(meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, Isobornyl (meth)acrylate, tridecyl (meth)acrylate, polycarprolactone (meth)acrylate, phenoxy tetraethylene glycol (meth)acrylate and imide acrylate.

15 The difunctional nonfluorinated (meth)acrylate which may be employed in the present invention may be ethoxylated nonylphenol (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,6-hexanediol
 20 di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, cyclohexane dimethanol di(meth)acrylate and tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate.

Preferred examples of the tri- or multi-functional nonfluorinated
 25 (meth)acrylate are tris[2-(acryloyloxy)ethyl]isocyanurate, trimethylol propane triacrylate, ethylene oxide added trimethylol propane triacrylate, pentaerythritol triacrylate, tris(acryloxyethyl)isocyanurate, dipentaerythritol hexaacrylate and caprolactone denatured dipentaerythritol hexaacrylate.

Representative examples of the photoreactive monomer (B₂) having at
 30 least one epoxy group include 3,4-epoxycyclohexylmethyl-3,4-epoxy cyclohexane carboxylate, bis-(3,4-epoxycyclohexyl)adipate, 3-ethyl-3-hydroxymethyl-oxetane, 1,2-epoxyhexadecane, alkyl glycidyl ether, 2-ethyl hexyl diglycol glycidyl ether, ethyleneglycol diglycidyl ether, diethyleneglycol diglycidyl ether, PEG#200 diglycidyl ether, PEG#400
 35 diglycidyl ether, propyleneglycol diglycidyl ether, tripropyleneglycol diglycidyl ether, PPG#400 diglycidyl ether, neopentylglycol diglycidyl ether,

1,6-hexanediol diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, diglycidyl ether of propyleneoxide modified bisphenol A, dibromo neopentylglycol diglycidyl ether and trimethylolpropane triglycidyl ether.

The photoreactive monomer may be employed in an amount of from 20
5 to 80 wt% based on the amount of the photocurable resin composition of the present invention.

(C) Photocurable initiator

A photocurable initiator which may be employed in the present
10 invention may preferably be Irgacure#184, Irgacure#907, Irgacure#500, Irgacure#651, Darocure#1173, Darocure#116, CGI#1800, CGI#1700, UVI-6990, UVI-6974, Sarcat CD1010, Sarcat CD1011, Sarcat CD1012, Sarcat K185 or a mixture thereof.

The initiator may be used in an amount of from 1 to 10 wt% based on
15 the amount of the photocurable resin composition of the present invention.

(D) Thermal stabilizer

Further, for the purpose of improving storage stability, various antioxidants and thermal stabilizer may be used.

20 A thermal stabilizer is used preferably in an amount of from 0.01 to 5 wt% based on the amount of the photocurable resin composition of the present invention.

(E) Antioxidant

25 The antioxidants include, for example, Irganox 1010, Irganox 1035, Irganox 1076 (Manufactured by Cibageigy Co. Ltd.) and a mixture thereof, which is used preferably in an amount of from 0.01 to 5 wt% based on the amount of the photocurable resin composition of the present invention.

30 The inventive photocurable resin composition for optical waveguides of the present invention may be prepared by a conventional method. A preferred embodiment of the process is as follows: a mixture of the ingredients (A) to (E) is added to a polymerization reactor at a temperature ranging from 15 to 50°C under a relative humidity of 60% or below and stirred at a rate in the range of
35 500 to 1000 rpm, to prepare a photocurable resin composition. If the temperature is less than 15°C, processing difficulties arise because the

viscosity of the oligomer(A) becomes too high, and if the temperature is higher than 50°C, the reaction product undergoes crosslinking.

The preparation of the photocurable resin composition may be controlled so that the composition has a refractive index ranging from 1.38 to 1.54, and a viscosity ranging from 50 to 2000 cps. Further, the inventive resin composition has excellent storage stability, a thermal decomposition temperature being as high as about 300°C, and a birefringence of 1×10^{-4} or below.

The fluorinated photocurable resin composition of the present invention also has an optical transmittance of 90% or more in the optical communication wavelength region, i.e., 0.85 μ m, 1.3 μ m and 1.55 μ m, respectively, and more particularly, having an optical loss of about 0.3 dB/cm at a wavelength of 0.85 μ m. Further, the inventive photocurable resin composition may be cured simply by UV irradiation at room temperature instead of the heat-curing method used for curing conventional resin compositions.

The present invention also provides a preparation method of an optical waveguide made of the inventive photocurable resin composition which comprises: coating the photocurable resin composition of the present invention as a under-cladding layer on a silicon wafer and photocuring the coated under-cladding layer by UV irradiation; coating the photocurable resin composition of the present invention as a core layer on a siloxane mold having an etched core pattern; placing the surface of the resin core pattern layer on the siloxane mold in close contact with the under-cladding layer coated on the silicon wafer, photocuring the core layer by UV irradiation, and removing the siloxane mold; and coating the photocurable resin composition of the present invention as a upper-cladding layer on the core layer, and photocuring the upper-cladding layer by UV irradiation.

A preferred embodiment of the preparation of optical waveguides according to the present invention is as follows:

Referring to FIG. 1, a core pattern of a desired shape is formed on a substrate using a photoresist, and a layer of polydimethyl siloxane is coated on the substrate and left standing at room temperature to remove air bubbles therefrom. The polydimethyl siloxane on the substrate is then cured at a temperature ranging from 30 to 100°C for a time ranging from 2 to 10 hrs, and the substrate is removed to obtain a polydimethyl siloxane mold. The resulting siloxane mold is spin-coated with the photocurable resin composition,

so that the resin composition fills just the portion of the core pattern. The photocurable resin composition is coated as an under-cladding layer on a silicon wafer, the coated layer is photocured by UV irradiation, and the surface of the core resin layer coated on the siloxane mold is placed in close contact
5 with the under-cladding layer material. The resulting fabrication is photocured by UV irradiation, and then, the siloxane resin mold is removed. As an upper-cladding layer material, the inventive photocurable resin composition is coated on the core layer and photocured by UV irradiation, to obtain the optical waveguide. By using such a micro-transfer molding
10 method, optical waveguides may be prepared much more simply in a much shorter time than a conventional method. Further, the inventive method may easily prepare very big optical waveguides in size of i.e., 1mm x 1mm depending on the kind of the photoresist materials, and singlemode or multimode waveguides according to the core pattern.

15 The present invention is further described and illustrated in Examples provided below, which are, however, not intended to limit the scope of the present invention.

Preparation of Oligomers

20

Preparation 1

A mixture of 375.27g of a fluorinated polyether (Fluorolink E10, manufactured by Ausimount Co., Ltd., Italy) and 89.38g of isoporondiisocyanate(IPDI) was heated to a temperature ranging from 40 to
25 60°C, followed by addition of 0.10g of n-butyltinlaurate(DBTL) with stirring at a rate of 200 to 300 rpm. The reaction was allowed to proceed at about 75°C until the -OH peak was not detectable by IR spectroscopy. 0.13g of hydroquinonemonomethylether(HQMME) and 34.85g of 2-hydroxyethylmethacrylate(2-HEMA) were added thereto, and the mixture
30 was reacted at about 80°C until the -NCO peak was not detectable by IR spectroscopy, to obtain a fluorinated photocurable urethane oligomer.

Preparations 2-13

The procedure of Preparation 1 was repeated using the ingredients
35 shown in Table 1, to obtain various fluorinated urethane oligomers.

- 11 -

Table 1

Prep.	(a) Polyol		(b) Diisocyanate		(c) Hydroxy (meth)acrylate or Hydroxy epoxy	
1	Fluorolink E10	375.27g	IPDI	89.38g	2-HEMA	34.85g
2	Fluorolink E	405.53g		67.61g		26.36g
3	Fluorolink D10/H	368.23g		94.45g		36.82g
4	Fluorolink D	375.27g		89.38g		34.85g
5	Fluorolink D10	368.23g		94.45g		36.82g
6	Fluorolink E10	368.74g	TMXDI	96.52g	2-HEMA	34.24g
7		391.76g	HDI	71.36g		36.38g
8		375.97g	HMDI	88.62g		34.91g
9		177.94g	poly(1,4-butanedio l)tolylene2,4-diisoc yanate terminated	305.04g		16.52g
10		390.45g	2,4-toluene diisocyanate	72.79g		36.26g
11		375.27g	IPDI	89.38g	2-HPA	38.9g
12		367.39g		87.50g	4-hydroxy cyclohexy lacrylate	44.61g
13		386.68g		92.10g	glycidol	20.72g

IPDI: isoporon diisocyanate, TMXDI: tetramethylxylene diisocyanate,
HDI: hexane diisocyanate, HMDI: 4,4'-dicyclohexylmethane diisocyanate,
2-HEMA: 2-hydroxyethylmethacrylate, 2-HPA: 2-hydroxypropylacrylate

5

Preparation of the Resin Composition for Optical Waveguides

Examples 1-10 and Comparative Example 1

The ingredients, (A) to (D), described in Table 2 and Z-6030 (Dow
10 Corning Co., Ltd.) as an additive were added to a reactor with stirring at a rate
of 300 ~ 1000 rpm at about 25°C under a relative humidity ranging from 30 to
60%, to obtain various fluorinated photocurable resin compositions.

Table 2

	Example										Comp. Exam. 1
	1	2	3	4	5	6	7	8	9	10	
(A) Oligomer											
Prep. 1	40	40									
Prep. 3			40	40							
Prep. 4					40	40					
Prep. 6							40	40			
Prep. 11									40	40	
UVE-150 ^{*1}											40
(B) Photoreactive monomer											
SR-339 ^{*2}	25	35	20	30	20	30	25	35	20	30	20
^{*3}	25	15	20	20	20	20	25	15	20	20	10
^{*4}			10		10				10		20
(C) Photo initiator											
Darocure#1173 ^{*5}	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
(D) Thermal Stabilizer											
BHT ^{*6}	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Z-6030	5	5	5	5	5	5	5	5	5	5	5
TOTAL	100	100	100	100	100	100	100	100	100	100	100

*1: Croda Co., Ltd.,

*2: Sartomer Co., Ltd.,

*3: 2-perfluorooctylethylacrylate,

*4: 2-hydroxypropylacrylate,

*5: Cibar Geigy Co., Ltd.,

5 *6: 2,6-di-tert-butyl-4-methylphenol(Aldrich Chemical Co., Ltd.)

Physical Characteristics

The properties of the resin compositions prepared in Examples 1-10 and Comparative Example 1 were measured with the methods described below, and the results are shown in Table 3:

(1) Inherent viscosity: measured by a Brookfield viscometer (No. 41 spindle) at 25°C.

(2) Refractive index of uncured resin composition

15 The refractive index of each resin composition was obtained using an

Abbe Refractometer with a sodium d-line (wavelength 589.3 μ m) at 23°C.

(3) Refractive index (cured film)

Each composition was spin-coated on a silicon wafer for 20~30 seconds at 1500-3000 rpm, the coated resin was photocured with 100 mJ/cm² UV using a fusion lamp, and further cured at a temperature ranging from 60 to 100°C for over 10 minutes, to obtain a film coated on the silicon wafer. The refractive index of the cured film having a thickness of 2-15 μ m was measured at a wavelength of 850nm with Prism-Coupler (manufactured by Sairon Co., Ltd.). The difference($\Delta(n_{TE}-n_{TM})$) between the refractive index(n_{TE}) in an electric field mode and the refractive index(n_{TM}) in a magnetic field mode represents the birefringence of the coated film.

(4) Optical transmittance (%T)

Each resin composition was coated on a glass substrate to a thickness of 150 μ m, and cured by irradiating thereon 100 mJ/cm² UV and subsequently, heat-cured at 60 to 100°C for over 10 minutes, to obtain a cured resin film. Then a film sample (size: 3cm x 3cm) was stripped off from the substrate, and the optical transmittance thereof was measured at 600 ~ 1600nm with a UV-VIS-NIR spectrophotometer (manufactured by Varian Co., Australia).

(5) Hardness (A or D): the hardness of the specimen (size: 50mm x 20mm x 5mm) cured in the same condition as the optical transmittance measurement was measured with Shore Durometer Hardness.

(6) Curing shrinkage (%): measured according to ASTM D-792

(7) Glass transition temperature (T_g): the specimen used in the optical transmittance measurement was subjected to T_g measurement at a temperature progress rate of 10°C/min in the range of 25 to 250°C using a dynamic mechanical thermal analyzer (DMTA).

(8) Thermal decomposition temperature (T_d): measured under a nitrogen atmosphere at a temperature progress rate of 10°C/min in the range of 25 to 700°C with a thermogravimetric analyzer (TGA).

(9) Storage stability: the appearance after the resin composition was stored at room temperature for 6 months was observed.

(10) Optical loss (dB/cm): A material having a refractive index lower than that of the cured film of a sample composition was coated on a silicon wafer, and then, the composition was coated thereon, followed by curing as in the preparation of the specimen employed in the Refractive index (film)

measurement. The resulting cured film was subjected to optical loss measurement with a prism-coupler (manufactured by Sairon Co., Ltd.).

Table 3

	Example										Com.
	1	2	3	4	5	6	7	8	9	10	1
Liquid Type											
Viscosity(cPs)	250	350	150	200	250	350	350	450	250	350	300
Refractive Index	1.414	1.434	1.405	1.425	1.392	1.412	1.440	1.452	1.423	1.440	1.481
Film Type											
Refractive Index											
nTE	1.427	1.447	1.418	1.438	1.405	1.425	1.453	1.465	1.436	1.453	1.494
nTM	1.427	1.447	1.418	1.438	1.405	1.425	1.453	1.465	1.436	1.453	1.493
Δ	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Optical Trans(%)	93	92	91	90	91	90	92	91	93	92	90
Hardness	38D	65D	75D	80D	80D	85D	70D	75D	40D	70D	85D
CuringShrink.(%)	8	7	8	8	8	7	8	8	8	7	9
Tg (°C)	93	120	99	118	102	122	100	130	94	120	90
Td (°C)	300	310	290	280	300	310	310	315	300	310	300
Storage Stability	good	good	good	good	good	good	change	change	good	good	change
Optical Loss(dB/cm)	0.243	0.241	0.251	0.254	0.264	0.267	0.314	0.324	0.243	0.241	0.813

5 Preparation of Optical Waveguides

Example 11

The fluorinated resin composition prepared in Example 1 was spin-coated at 3000 rpm for 30 seconds as a cladding layer on a silicon wafer, and photocured with 100mJ/cm² UV using a fusion lamp, a 300W mercury lamp, at room temperature for 5 to 15 minutes and successively heat-cured at 60 to 100°C for over 10 minutes. A substrate having a desired core pattern formed thereon was prepared by photoresist, and a layer of polydimethyl siloxane was coated thereon, and left standing at room temperature to remove air bubbles thereof. The siloxane resin was cured at 40°C for 2 hrs, and then the resulting cured siloxane resin was stripped from the substrate, to obtain a cured siloxane resin mold (core size: 45μm). The resulting cured siloxane resin mold was spin-coated with the photocurable resin composition obtained

in Example 2, so that the resin composition filled the pattern portion of the mold. The coated siloxane resin mold was placed on the cladding layer coated silicon wafer, in such a way that the face of the filled pattern case in close contact with the cladding layer. The resulting fabrication was cured
 5 with 100 mJ/cm² UV using a fusion lamp at room temperature for a time ranging from 5 to 15 minutes and successively heat-cured at a temperature ranging from 60 to 100°C for over 10 minutes, followed by detaching the siloxane resin mold. The optical microscope and scanning electron microscope photographs of the cross-sectional view of the core-layer are
 10 shown in FIG. 2a and 2b, respectively. As an upper-cladding layer, the resin composition prepared in Example 1 was spin-coated at 1000 rpm for 20 seconds on the surface of the core layer, and photocured with 100 mJ/cm² UV at room temperature and successively curing at a temperature ranging from 60 to 100°C for over 10 minutes, to obtain a photocurable optical waveguide.

15

Example 12

The procedure of Example 11 was repeated using the resin compositions obtained in Example 3 and 4 in place of the compositions of Example 1 and 2, respectively, to obtain a photocurable optical waveguide.

20

Physical Characteristics of Optical Waveguides

The physical characteristics of the photocurable optical waveguides obtained in Example 11 and 12 were measured, and the results are shown in
 25 Table 4, wherein Propagation loss was measured using a cut-back method at a wavelength of 850nm.

Table 4

	Example 11	Example 12
Waveguide type	Buried type	Buried type
Refractive index difference (%)	1.39%	1.40%
Core size	45μm x 45μm	45μm x 45μm
Propagation loss (dB/cm)	0.245	0.214

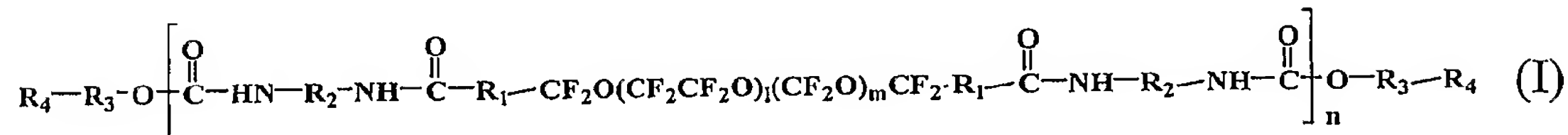
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As can be seen from the above results, the fluorinated resin composition for optical waveguides comprising a fluorinated photocurable urethane oligomer having at least one (meth)acryloyl group in accordance with the present invention has higher optical transmittance, thermal stability and storage
5 lifetime in addition to lower birefringence, and optical waveguides may be more simply made of the inventive composition via micro-molding technique which does not need a conventional etching process but only UV irradiation.

While the subject invention has been described and illustrated with respect to the preferred embodiments only, various changes and modifications
10 may be made therein without departing from the inventive concept of the present invention which should be limited only by the scope of the appended claims.

What is claimed is:

1. A fluorinated photocurable urethane oligomer of formula (I):



- 5 wherein:

R_1 is $-\text{CH}_2\text{O}-$ or $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_m\text{O}-$;

R_2 is an aromatic or aliphatic hydrocarbon group containing from 6 to 100 carbon atoms;

R_3 is an aromatic or aliphatic hydrocarbon group containing from 2 to 10 10 carbon atoms; and

R_4 is a (meth)acrylate or epoxy group.

2. A photocurable resin composition for use in producing an optical waveguide comprising the fluorinated urethane oligomer of formula (I) of 15 claim 1, a reactive monomer and a photocurable initiator.

3. The photocurable resin composition of claim 2, wherein the fluorinated urethane oligomer is prepared by reacting a polyol with a diisocyanate in the present of an urethane reaction catalyst, and reacting the resulting product with 20 a hydroxy (meth)acrylate having at least one (meth)acryloyl group and one hydroxy group, or a hydroxy epoxy having at least one epoxy group and one hydroxy group in the presence of an urethane reaction catalyst and a polymerization inhibitor.

- 25 4. The photocurable resin composition of claim 3, wherein the polyol has an average molecular weight ranging from 500 to 10,000, and includes a fluorinated perfluoropolyether polyol or a perfluoropolyether polyol having a nonfluorinated polyether group attached at an end of the perfluoropolyether chain.

30

5. The photocurable resin composition of claim 3, wherein the diisocyanate is selected from the group consisting of isophoron diisocyanate(IPDI), 1,6-hexane diisocyanate(HDI), 1,8-octamethylene diisocyanate, tetramethylxylene diisocyanate(TMEDI),

4,4'-dicyclohexylmethane diisocyanate(HMDI), 4,4'-diphenylmethane
 diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate,
 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate,
 4-bromo-6-methyl-1,3-phenylene diisocyanate,
 5 4-chloro-6-methyl-1,3-phenylene diisocyanate, poly(1,4-butanediol)tolylene
 2,4-diisocyanate terminated, poly(1,4-butanediol)isophorone diisocyanate
 terminated, poly(ethylene adipate)tolylene 2,4-diisocyanate terminated;
 poly[1,4-phenylene diisocyanate-co-poly(1,4-butanediol)] diisocyanate,
 poly(hexamethylene diisocyanate, poly(propylene glycol)tolylene
 10 2,4-diisocyanate terminated, poly(tetrafluoroethylene
 oxide-co-difluoromethylene oxide) α,ω -diisocyanate, 2,4-toluene
 diisocyanate, 2,5-toluene diisocyanate, 2,6-toluene diisocyanate,
 1,5-naphthalene diisocyanate and a mixture thereof.

15 6. The photocurable resin composition of claim 3, wherein the hydroxy
 (meth)acrylate having at least one (meth)acryloyl group and one hydroxy
 group is selected from the group consisting of 2-hydroxyethyl(meth)acrylate,
 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate,
 1-hydroxybutyl(meth)acrylate, 2-hydroxy-3-phenyloxypropyl(meth)acrylate,
 20 neopentylglycolmono(meth)acrylate, 4-hydroxycyclohexyl(meth)acrylate,
 1,6-hexanediolmono(meth)acrylate, pentaerythritolpenta(meth)acrylate,
 dipentaerythritolpenta(meth)acrylate, 2-methacryloxyethyl 2-hydroxy propyl
 phthalate, glycerin di(meth)acrylate, 2-hydroxy-3-acryloyloxy
 propyl(meth)acrylate, polycaprolactone polyol mono(meth)acrylate and a
 25 mixture thereof.

7. The photocurable resin composition of claim 3, wherein the hydroxy
 epoxy having at least one epoxy group and one hydroxy group is glycidol or
 epoxidized tetrahydrobenzyl alcohol.

30

8. The photocurable resin composition of claim 2, wherein the
 photoreactive monomer is a (meth)acrylate having at least one (meth)acryloyl
 group or a photoreactive monomer having at least one epoxy group.

35 9. The photocurable resin composition of claim 8, wherein the
 (meth)acrylate is a fluorinated (meth)acrylate or a nonfluorinated

(meth)acrylate, the fluorinated (meth)acrylate being selected from the group consisting of 2-perfluorooctylethyl acrylate, 2-perfluorooctylethyl methacrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, trifluoroethyl methacrylate, 5 2-perfluoroalkylethyl acrylate and 2-perfluoroalkylethyl methacrylate, and the nonfluorinated (meth)acrylate being selected from the group consisting of 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 1-hydroxybutyl(meth)acrylate, 2-hydroxy-3-phenyloxypropyl(meth)acrylate, tetrahydrofurfuryl 10 (meth)acrylate, isodecyl (meth)acrylate, 2-(2-ethoxyethoxy) ethyl(meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, isobornyl (meth)acrylate, tridecyl (meth)acrylate, polycarprolactone (meth)acrylate, phenoxy tetraethylene glycol (meth)acrylate, imide acrylate, ethoxylated nonyl phenol acrylate, 15 ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, cyclohexane dimethanol 20 di(meth)acrylate, tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate, tris[2-(acryloyloxy)ethyl]isocyanurate, trimethylol propane triacrylate, ethylene oxide-3mole-added trimethylol propane triacrylate, ethylene oxide-6mole-added trimethylol propane triacrylate, pentaerythritol triacrylate, tris(acryloxyethyl)isocyanurate, dipentaerythritol hexaacrylate and 25 caprolactone denatured dipentaerythritol hexaacrylate.

10. The photocurable resin composition of claim 8, wherein the photoreactive monomer having at least one epoxy group is selected from the group consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxy cyclohexane 30 carboxylate, bis-(3,4-epoxycyclohexyl)adipate, 3-ethyl-3-hydroxymethyl-oxetane, 1,2-epoxyhexadecane, alkyl glycidyl ether, 2-ethylhexyl diglycol glycidyl ether, ethyleneglycol diglycidyl ether, diethyleneglycol diglycidyl ether, PEG#200 diglycidyl ether, PEG#400 diglycidyl ether, propyleneglycol diglycidyl ether, tripropyleneglycol 35 diglycidyl ether, PPG#400 diglycidyl ether, neopentylglycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, hydrogenated bisphenol A diglycidyl ether,

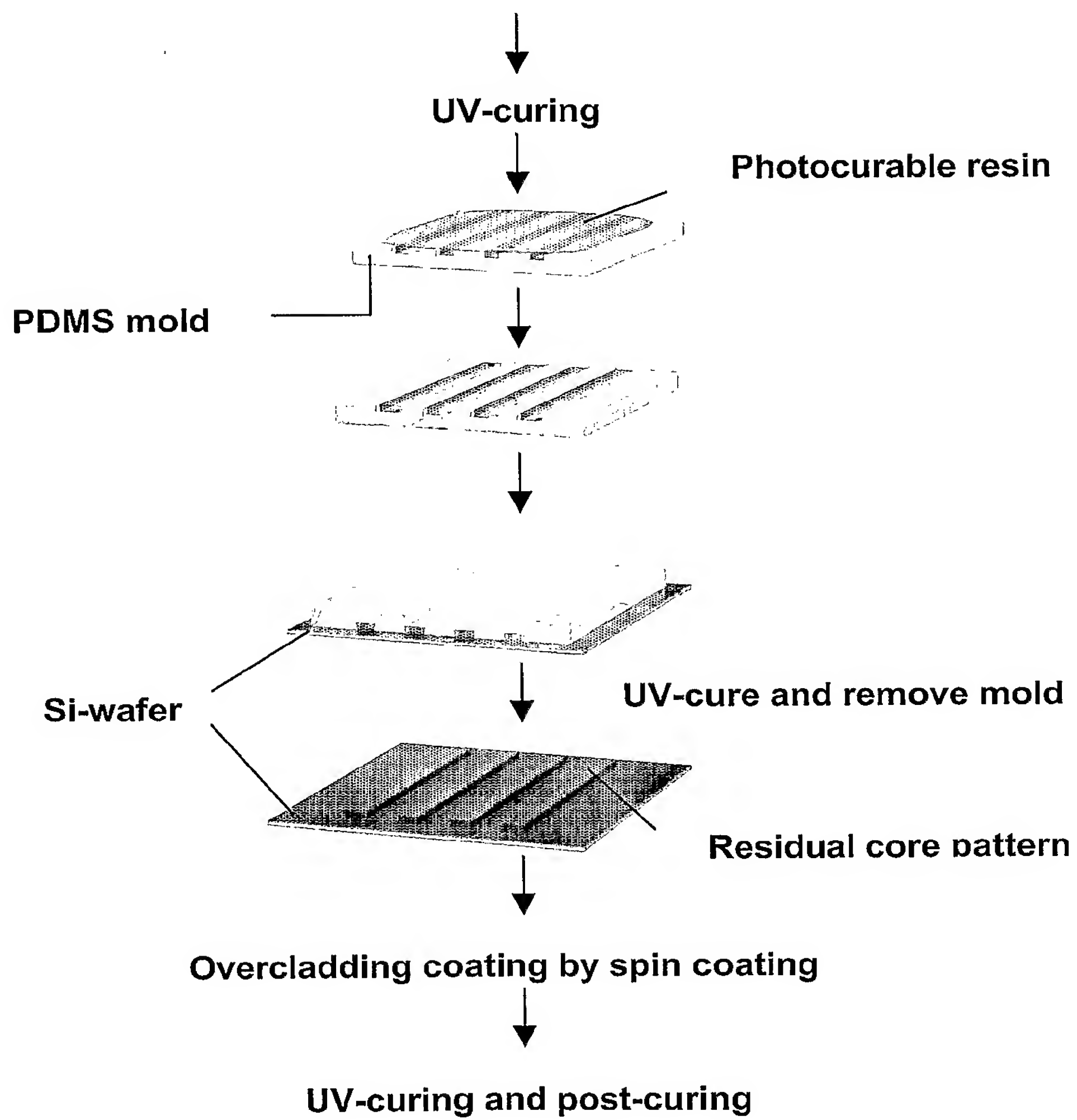
diglycidyl ether of propyleneoxide modified bisphenol A, dibromo neopentylglycol diglycidyl ether and trimethylolpropane triglycidyl ether.

11. The photocurable resin composition of any one of claims 2 to 10, which
5 has a birefringence of 1×10^{-4} or below, a thermal decomposition temperature of 300°C or higher, a controllable refractive index in the range from 1.38 to 1.54 and a controllable viscosity in the range from 50 to 2000 cps.
12. A method for preparing an optical waveguide, which comprises: coating
10 the photocurable resin composition of any one of claims 2 to 10 as a under-cladding layer on a silicon wafer and photocuring the coated layer by UV irradiation; coating the photocurable resin composition as a core layer on a siloxane mold having an etched core pattern; placing the surface of the core layer coated on the siloxane mold in close contact with the under-cladding
15 layer coated on the silicon wafer, photocuring the core layer by UV irradiation and removing the siloxane mold; and coating the photocurable resin composition as an upper-cladding layer on the core layer and photocuring the upper-cladding layer by UV irradiation.
- 20 13. An optical waveguide prepared by the method of claim 12.

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FIG. 1

Undercladding coating by spin coating

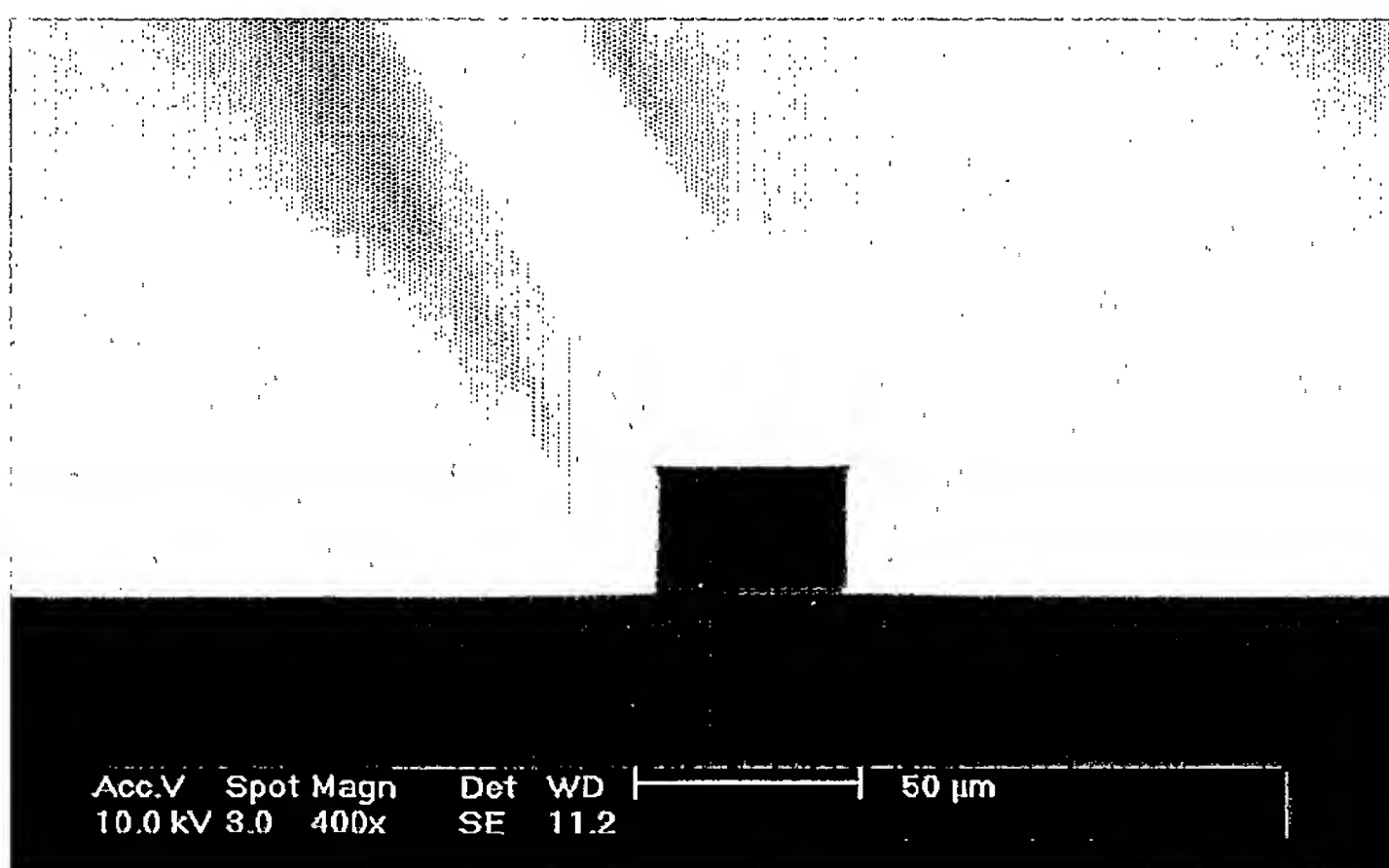


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FIG. 2a



FIG. 2b



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR02/02381**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 C08G 18/42**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 18/42, C09J 4/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patent and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA-on CD, KIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,017,603 A (NIPPON KAYAKU KABUSHIKI KAISHA) Jan. 25, 2000 see the whole documents	1-13
A	JP 12-63766 A (JSR CORP, NIPPON TOKUSHU COATING KK) Feb. 29, 2000 see the whole documents	1-13
A	WO 96/23828A1(DSM N.V) Aug. 08, 1996 see the whole documents	1-10
A	JP 10-237392 A (SHOWA DENKO KK) Sep. 08, 1998 see the whole documents	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

07 APRIL 2003 (07.04.2003)

Date of mailing of the international search report

07 APRIL 2003 (07.04.2003)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR02/02381

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JP 10-237392 A	Sep. 08, 1998	None	